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Manufacturing Process of Sodium Hydroxide and Nitric Acid from Thermochemically Split Sodium Nitrate

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For the manufacture of sodium hydroxide and nitric acid a new thermochemical process of splitting sodium nitrate has been proposed which consists of (i) splitting of sodium nitrate by iron(III) oxide, (ii) hydrolysis of sodium ferrate, and (iii) absorption of nitrogen dioxide into water. Key reactions (i) and (ii) have experimentally been verified. The overall heat requirement for the process is discussed on the basis of a material and heat flow-sheet of the process constructed.

Electricity has been rising in cost in many countries, particularly in Japan, since the first and second international rises in the price of crude oil. As a result, new energy-saving processes have been required for the manufacture of sodium hydroxide in place of the conventional electrolytic process of sodium chloride which consumes much electric energy.

There were two industrially practised processes of manufacturing sodium hydroxide except the conventional electrolytic process. Both of them used Na_2CO_3 as a raw material. As generally known, one of them was the oldest manufacturing process of NaOH that utilized a double decomposition reaction between Na_2CO_3 and $Ca(OH)_2$. Although this process was simple, it could only produce a dilute aqueous solution of NaOH with a poor conversion rate from carbonate to hydroxide. For instance, it produced a sodium hydroxide solution of 10—11 wt% with a conversion rate of about 90%. The other process was called the Löwig process.[1] This consisted of two reactions, one producing sodium ferrate through an interaction between Na_2CO_3 and Fe_2O_3 and the other being a hydrolysis of sodium ferrate to produce NaOH. The Löwig process had two merits: the first was that Fe_2O_3 used in the process could be reused without being consumed; the second was that a sodium hydroxide solution of about 30 wt% formed was industrially available. However, this process released CO_2 into the atmosphere. This is not preferable nowadays from a viewpoint of the prevention of global atmospheric pollution.

The process to be proposed in this study will neither release any gases into the atmosphere, nor produce any unnecessary by-products. The sodium hydroxide aqueous solution to be formed is industrially available in the respect of concentration, as with the Löwig process. In addition, the raw materials for this process are only $NaNO_3$ and H_2O. As generally known, $NaNO_3$ is contained in large quantity in Chile saltpeter which is an abundant natural resource in Chile and Peru.

The thermochemical splitting process of $NaNO_3$ proposed here is composed of the three chemical reactions

$$NaNO_3 + 1/2Fe_2O_3 \longrightarrow NaFeO_2 + NO_2 + 1/4O_2, \tag{1}$$

$$NaFeO_2 + 1/2H_2O \longrightarrow NaOH + 1/2Fe_2O_3, \tag{2}$$

$$NO_2 + 1/4O_2 + 1/2H_2O \longrightarrow HNO_3, \tag{3}$$

which sequence leads to the overall reaction

$$NaNO_3 + H_2O \longrightarrow NaOH + HNO_3. \tag{4}$$

Fe_2O_3 circulates between Reactions 1 and 2. Reaction 3 is the same as the absorption step of NO_2 into water in the current manufacturing process of nitric acid.

The object of the present work is divided into two: (1) Characterization and experimental verification of the reactions concerning the proposed process, and (2) construction of the material and heat flow-sheet to estimate the overall heat requirement for the manufacture of NaOH and HNO_3 by this thermochemical process.

Reaction Characteristics and Experimental Verification

Reaction 1. *Thermal Analysis*: Mixtures of $NaNO_3 + xFe_2O_3$ (x=0—1.0) were analyzed by DTA from 25 to 1000 °C in a stream of nitrogen at a heating rate of 300 °C/h. Every mixture used for the thermal analysis was 100 mg in a shape of powder. Powdered iron(III) oxide used was identified with hematite by X-ray diffraction pattern, and its particle size was 75—105 μm for 64 wt% and less than 46 μm for the rest. DTA curves were obtained by use of a differential thermal analyzer (Type TA3-L, Chyo Balance Corporation, Japan). Results are shown in Fig. 1. The endothermic peaks at 278 and 308 °C on every DTA curve in Fig. 1 correspond to the transition and fusion of $NaNO_3$.[2] Every curve shows a gradual endothermic peak over 400 °C which shifts to higher temperatures with increasing content of $NaNO_3$ in mixtures. The peaks for the mixtures at 600—700 °C indicate the end of reaction more clearly than the peak for pure $NaNO_3$. Both pure $NaNO_3$ and the mixtures, however, have similar patterns in their DTA curves. Therefore, it is estimated from

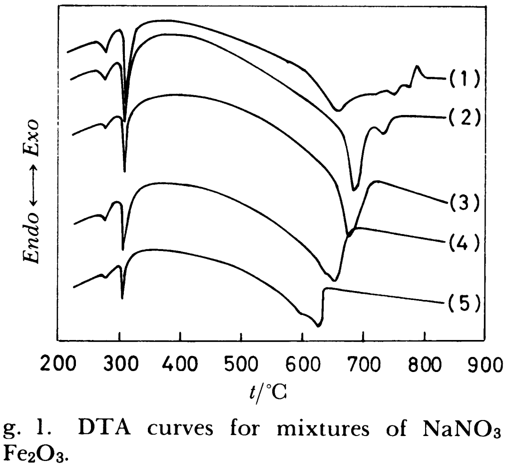

Fig. 1. DTA curves for mixtures of $NaNO_3$ and Fe_2O_3.
Heating rate: 5 °C/min, Atmosphere: N_2 50 ml/min.
$NaNO_3/Fe_2O_3$=(1): pure $NaNO_3$, (2): 2.5, (3): 2.0, (4): 1.5, (5): 1.0.

the thermal analysis that Reaction 1 is essentially a decomposition of $NaNO_3$ in conjunction with Fe_2O_3.

X-Ray Analysis: In order to grasp the outline of Reaction 1, an X-ray analysis was conducted with the solid phase. Mixed samples of $NaNO_3$ and Fe_2O_3 with various molar ratios ($NaNO_3/Fe_2O_3=1.0$, 1.5, 2.0, and 2.5) were heated in a platinum boat in an atmosphere of air at 950, 1000, and 1050 K. Each of solid residues was examined by X-ray analysis. X-Ray diffraction patterns were obtained by use of an X-ray diffractometer (Type Geigerflex RAD-III A, Rigaku Denki Corporation, Japan).

The solid residues obtained at 1050 K from every mixture showed only the X-ray pattern of $NaFeO_2$ except the unchanged Fe_2O_3. The solid residues obtained at 950 and 1000 K from the mixtures with molar ratios $NaNO_3/Fe_2O_3=2.0$ and 2.5 showed the X-ray patterns of both Na_3FeO_3 and $NaFeO_2$. $NaFeO_2$ may be regarded as the general component of the solid residues formed at 1050 K from the mixtures with molar ratios less than 2.0 of $NaNO_3/Fe_2O_3$, as far as the results of X-ray analysis is concerned.

Conversion Rate: Conversion rates from $NaNO_3$ to $NaFeO_2$ were determined at various reaction times. With the apparatus shown in Fig. 2, a mixture with a molar ratio $NaNO_3/Fe_2O_3=2.0$ in a platinum boat was heated in still or flowing air of 500 ml/min at 1 atm for a prescribed time. Then the solid residue in the platinum boat was hydrolyzed in boiling water to form NaOH. The amount in mole of the determined NaOH was regarded as equivalent to that of the $NaFeO_2$ formed by Reaction 1. The NaOH formed was determined by neutralization.

Results are shown in Figs. 3 and 4. As shown in Fig. 3, the reaction proceeds in still air at 1050 K faster than at 950 and 1000 K. In flowing air, however, as seen from Fig. 4, the reaction rate increased at 950 and 1000 K but was almost the same at 1050 K as in still air. This is because the total pressure of evolved vapor is more than 1 atm at 1050 K, whereas it is below 1 atm at 950 and 1000 K. The conversion rate does not reach 100% in either of the atmospheres of still and flowing airs at 1 atm. The maximum conversion rate is 95—96% in all the experimental conditions of this study.

In order to disclose the reason, amounts of evolved gas with Reaction 1 were determined.

Evolved Gas: About 2 g of a mixture ($NaNO_3/Fe_2O_3=2.0$ in molar ratio) in a platinum boat was heated for 30 min at 1050 K in an atmosphere of flowing O_2 and the evolved gas was allowed to be absorbed into 450 ml of 0.26 mol/l NaOH aqueous solution as shown in Fig. 2. The amount of the residual sodium hydroxide in the solution after the absorption of evolved gas was determined by neutralization. The solid residue in the platinum boat was hydrolyzed, and the NaOH formed was determined. According to the equilibrium constants[3] of the reaction $NO+1/2O_2 \rightleftarrows NO_2$, the species of nitrogen oxide in the evolved gas is NO at 1050 K but is NO_2 together with a large quantity of O_2 at room temperature where the gas is absorbed. Thus, the amount of absorbed NO_2 in coexistence with O_2 was compared with the initial amount of $NaNO_3$ for the determination of conversion rate on the basis of evolved NO_2. The result is shown in Fig. 5. As is clear from Fig. 5, the conversion rate on the basis of evolved NO_2 is almost 100% over the range 50—400 ml/min of oxygen flow, whereas that on the basis of formed NaOH is about 96% at the maximum. The drop in conversion rate at 500 ml/min of O_2 flow in Fig. 5 may be due to the fact that

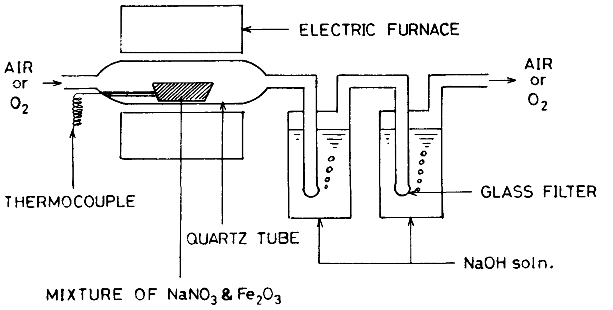

Fig. 2. Apparatus for reaction of splitting $NaNO_3$ with Fe_2O_3.

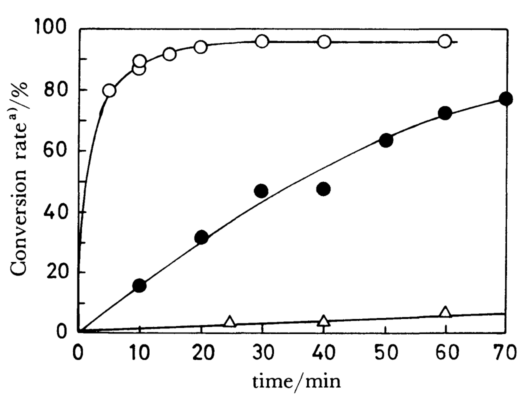

Fig. 3. Conversion rates of Reaction 1 at the various reaction times in still air.

○: 1050°K, ●: 1000°K, △: 950°K.

$$a)\ \frac{\text{moles of formed NaOH}}{\text{moles of initial } NaNO_3} \times 100$$

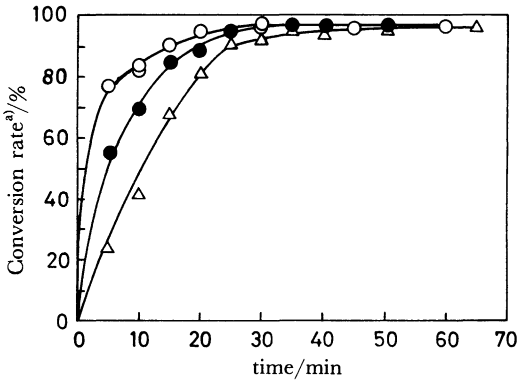

Fig. 4. Conversion rates of Reaction 1 at the various reaction times in flowing air of 500 ml/min. ○: 1050°K, ●: 1000°K, △: 950°K.

a) Defined in the same manner as in Fig. 3.

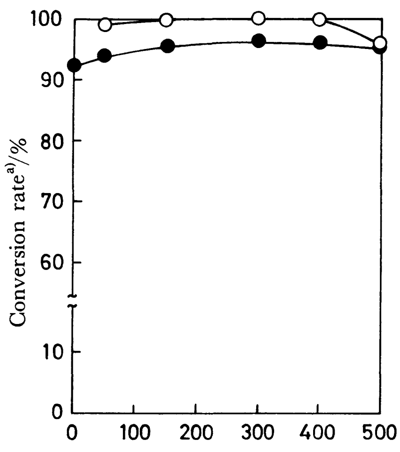

Fig. 5. Conversion rates of Reaction 1 on the bases of evolved NO_2(○), and of formed NaOH(●) at 1050°K under an atmospher of O_2.

NO_2 goes out of the absorbing solution with the flowing O_2 without being absorbed into the solution.

Reaction 2 (Hydrolysis of $NaFeO_2$). As already clarified by X-ray analysis, the general component of solid residue with Reaction 1 is $NaFeO_2$ at 1050 K at molar ratios less than 2.0 of $NaNO_3/Fe_2O_3$. Therefore, this study is focused on the hydrolysis of $NaFeO_2$ formed at 1050 K with Reaction 1.

Three samples of $NaFeO_2$ were hydrolyzed for the purpose of determining the maximum yield of NaOH from $NaFeO_2$. They were prepared at 1050 K in the respective molar ratios of $NaNO_3/Fe_2O_3$=1.0, 1.5, and 2.0.

Each sample of 1.3 g was added into a water of about 100 g and the suspended solution was boiled off down to half the volume with evaporation of water. After cooling, OH^- and CO_3^{2-} in the suspended solution were analyzed with an automatic titrator. As a result of this analysis, it was concluded that 95.4—96.4% of $NaFeO_2$ is converted to NaOH by hydrolysis with all the samples prepared from the mixtures with molar ratios $NaNO_3/Fe_2O_3$=1.0, 1.5, and 2.0, if 100% of the initial $NaNO_3$ is assumed to have been converted to $NaFeO_2$ in every preparation of the $NaFeO_2$ samples. In order to detect undecomposed $NaFeO_2$, an X-ray analysis was conducted on dry samples of solid residues after hydrolysis of $NaFeO_2$. However, any X-ray diffraction patterns assignable to sodium ferrate were not found; all the samples showed only the X-ray diffraction pattern of hematite.

For the purpose of investigating the mass balance of sodium with respect to Reactions 1 and 2, sodium was determined in three samples: (1) A solid residue from Reaction 1, (2) a solid residue after the hydrolysis of Reaction 2, and (3) solid sticks on the quartz tube wall and the SiO_2 powders around the platinum boat containing reactants for Reaction 1. The SiO_2 powders were used for catching vaporized $NaNO_3$, because $NaNO_3$ reacts with SiO_2.[2] The determination of sodium was conducted by flame emittion photometry after extraction of sodium ion into the aqueous solutions by decomposing the solids with hydrochloric acid, hydrofluoric acid, and perchloric acid. As a result, it was revealed that 95.4—96.4% of the sodium contained in the initial sodium nitrate forms $NaFeO_2$ which is easily hydrolyzed, and that 1.6—1.7% of the sodium coexists with Fe_2O_3 without forming NaOH after the hydrolysis of $NaFeO_2$. The residual percentage 1.9—3.0% of sodium is regarded as the $NaNO_3$ which vaporized without reacting with Fe_2O_3 during the heating step from room temperature to the reaction temperature. The vaporized $NaNO_3$ is probably caught during passage through the column packed with Fe_2O_3, because the sodium from vaporized $NaNO_3$ was detected in solid sticks on the quartz tube wall and the SiO_2 powders around the platinum boat. This vaporized $NaNO_3$ will, however, be regarded as lost in the later discussion of this paper, because it was not recovered in this study.

The hydrolysis rate of $NaFeO_2$ as a function of reaction time was also measured as shown in Fig. 6. A sample containing 0.2 g $NaFeO_2$ and 20 g water in a Teflon bottle was shaken and warmed in an oil bath at a constant controlled in temperature within ±0.1 °C. As seen from Fig. 6, features of hydrolysis rate with respect to reaction time are similar above 60 °C in that it takes as short as 30 min to reach the maximum hydrolysis rate. On the other hand, the hydrolysis of $NaFeO_2$ proceeds rather slowly below 50 °C. At any cases, the maximum hydrolysis rate is more than 98% in view of the already-stated fact that 1.9—3.0% of sodium in the initial $NaNO_3$ will not form $NaFeO_2$ in the step of preparation of the $NaFeO_2$ samples due to the vaporization of $NaNO_3$.

It is industrially important to clarify the achievable concentration of the sodium hydroxide aqueous solution obtainable by means of the hydrolysis of $NaFeO_2$. Figure 7 shows concentrations of sodium hydroxide aqueous solutions obtained with varied hydrolysis periods. In this experiment, the expected amount of water was added to each $NaFeO_2$ sample so that a sodium hydroxide solution of 50 wt% might be formed when the $NaFeO_2$ sample was perfectly hydrolyzed. The sodium hydroxide solutions were determined in concentration after they had been separated from iron(III) oxide by filtration with paper filters. As shown in Fig. 7, the concentration of sodium hydroxide solution reaches about 25 wt% at about 15 min from the start of hydrolysis, slowly increasing up to 28.5 wt% at 80 min from the start. Thus, these results suggests that the industrially achievable concentration of sodium hydroxide solution would be 25—28 wt%.

Reaction 3 (Production of HNO_3). The formation of nitric acid according to Eq. 3 is well known and quite similar to the absorption step of nitrogen dioxide into water in the current manufacturing process of nitric acid. This absorption step of nitrogen dioxide is successfully practical in many factories manufacturing nitric acid all over the world.

Thermodynamic Calculation

The enthalpy change (ΔH°_{298}), entropy change (ΔS°_{298}), and free energy change (ΔG°) for each of the reactions involved in the present process were calculated based on thermochemical data.[4,5] The results are shown in Table 1 and Fig. 8.

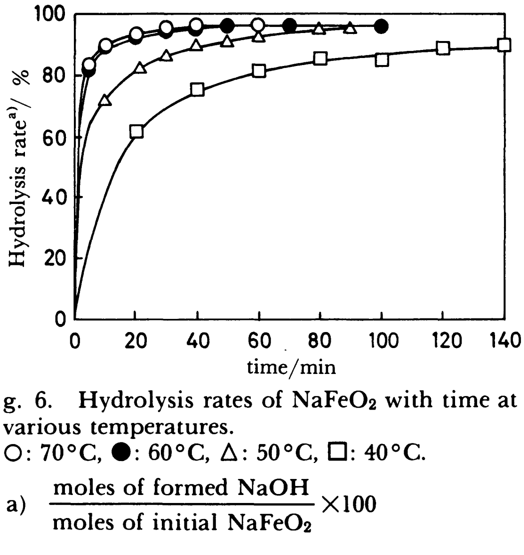

Fig. 6. Hydrolysis rates of $NaFeO_2$ with time at the various temperatures.
○: 70 °C, ●: 60 °C, △: 50 °C, □: 40 °C.

a) $\dfrac{\text{moles of formed NaOH}}{\text{moles of initial NaFeO}_2} \times 100$

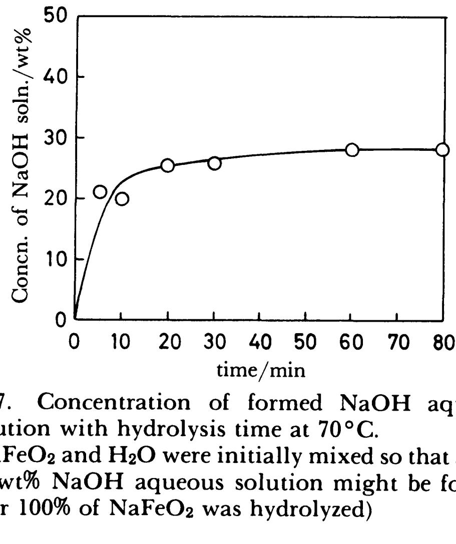

Fig. 7. Concentration of formed NaOH aqueous solution with hydrolysis time at 70 °C.
($NaFeO_2$ and H_2O were initially mixed so that about 50 wt% NaOH aqueous solution might be formed after 100% of $NaFeO_2$ was hydrolyzed)

Material and Heat Flow-sheet

An estimated material and heat flow-sheet for this process is shown in Fig. 9. In Fig. 9, R, E, and S refer to the reactor, heat exchanger, and separator, respectively. The other notations are as follows: the enthalpy change of reaction (ΔH°_T), the Gibbs free energy change (ΔG°_T), the heat input for heating the reactants ($Q_r = \Delta H^\circ_T - \Delta H^\circ_{298}$), and the heat output for cooling the products ($Q_P = \Delta H^\circ_T - \Delta H^\circ_{298}$).

The following assumptions were made for the construction of the flow-sheet:

$NaNO_3$ will be perfectly converted to $NaFeO_2$ with the stoichiometric ratio between $NaNO_3$ and Fe_2O_3. Q_P at E1 contains the reaction heat of $NO + 1/2O_2 \rightarrow NO_2$. The conversion rate for $NaFeO_2$ to NaOH will pessimistically be 95% at a molar ratio $H_2O/NaFeO_2 =$ 6.5 for the formation of 27 wt% sodium hydroxide aqueous solution. ΔG°_{343} and ΔH°_{343} at R2 contain the free energy and enthalpy changes for the dissolution[6] of NaOH into H_2O. The conversion rate for NO_2 to HNO_3 will be 100% at 298 K. The concentration of nitric acid aqueous solution formed will be 64%. Therefore, the heat of dilution from 100 to 64 wt% of nitric acid solution is contained in ΔH°_{298} at R3. The heat unit in the flow-sheet is kcal.

Table 1. Enthalpy, entropy, and free energy changes (ΔH°_{298}, ΔS°_{298}, and ΔG°) for reaction 1—3[a)]

Reaction	ΔH°_{298}/ kcal mol^{-1} b)	ΔS°_{298}/ cal mol^{-1} K^{-1} b)	ΔG°/ kcal mol^{-1} b)
1	+51.4	+52.4	−1.9 at 1050 K
2	−9.1	+9.9	−19.2 at 343 K
3	−20.3	−42.0	−7.9 at 298 K
Total	+22.0	+20.3	

a) (1) $NaNO_3(s,l) + 1/2Fe_2O_3(s) \rightarrow NaFeO_2(s) + NO_2(g) + 1/4O_2(g)$. $NaNO_3$: liquid>579 K≧solid.
(2) $NaFeO_2(s) + 1/2H_2O(l,g) \rightarrow NaOH\cdot 6aq + 1/2Fe_2O_3(s)$.
(3) $NO_2(g) + 1/4O_2(g) + 1/2H_2O(l,g) \rightarrow HNO_3\cdot 2aq$
b) 1 cal = 4.184 J.

Heat Requirement. The heat requirement (Q_{req}) for the process was calculated by using the equation[7–9] formulated on the basis of the flow-sheet in

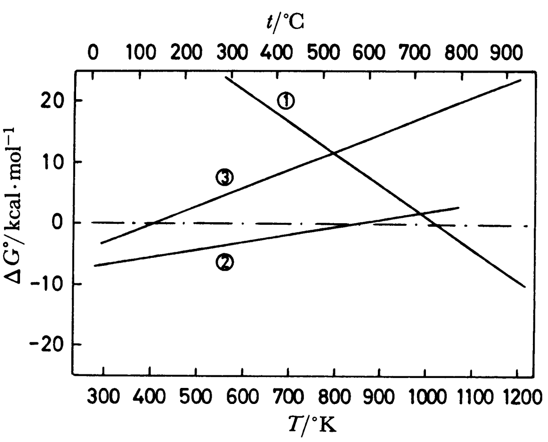

Fig. 8. Free energy change (ΔG°) *vs.* temperature plot for Reaction 1—3.
(1) $NaNO_3(s,l) + 1/2Fe_2O_3 \rightarrow NaFeO_2(s) + NO_2(g) + 1/4O_2(g)$ $NaNO_3$: liquid>579°K≧solid
(2) $NaFeO_2(s) + 1/2H_2O(l,g) \rightarrow NaOH\cdot 6aq + 1/2Fe_2O_3(s)$ H_2O: gas>373°K≧liquid
3) $NO_2(g) + 1/4O_2(g) + 1/2H_2O(l,g) \rightarrow HNO_3\cdot 2aq$

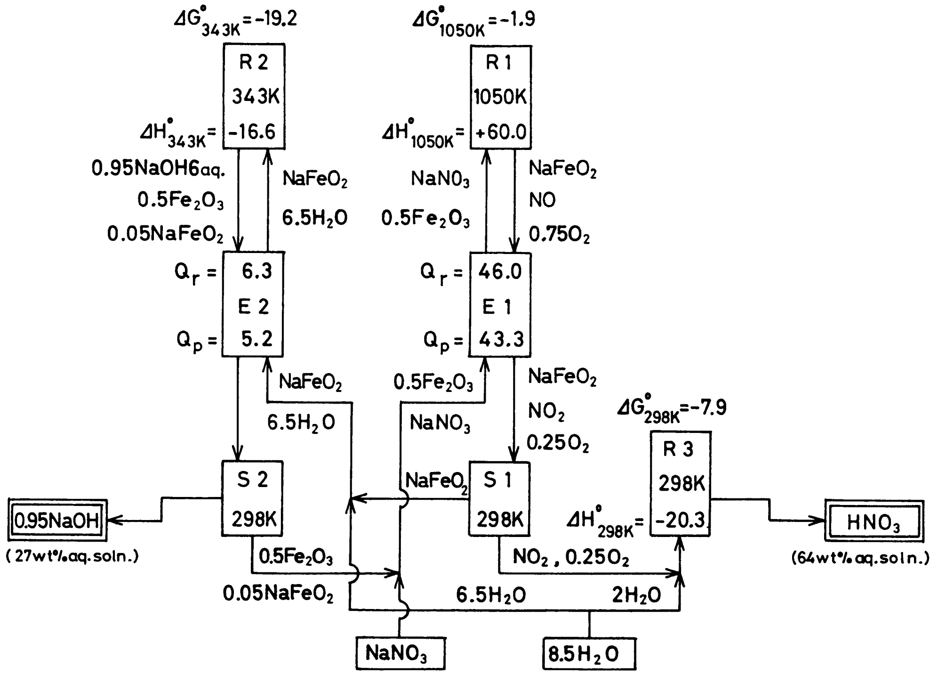

Fig. 9. Material and heat flow-sheet in a manufacturing process of NaOH and HNO_3 from thermochemically split $NaNO_3$.
R: reactor, E: heat exchanger, S: separator, Q_r: heat input for heating the reactants ($Q_r = \Delta H^\circ_T - \Delta H^\circ_{298K}$) Q_P: heat output for cooling the products ($Q_P = \Delta H^\circ_T - \Delta H^\circ_{298K}$)
(the heat unit in the flow-sheet is kcal)

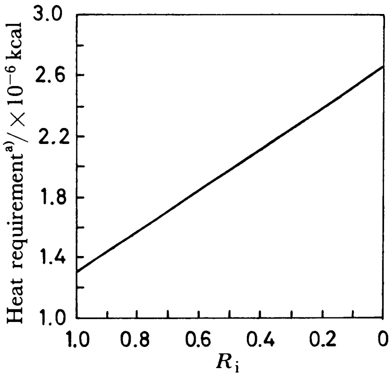

Fig. 10. Heat requirement of the thermochemical process of manufacturing NaOH and HNO_3 from $NaNO_3$.
a) Heat required in manufacturing 27 wt% NaOH aqueous solution containing NaOH of 1.000 ton, and 64 wt% HNO_3 aqueous solution containing HNO_3 of 1.658 ton.

$$Q_{req} = \sum(\Delta H^\circ_T + Q_r) - \sum Q_p \times R_i \qquad (5)$$

Fig. 9, where R_i represents the ratio for the thermal regeneration. Figure 10 shows the change of the heat requirement with values of R_i. The heat requirement in Fig. 10 represents values applicable to a manufacture of 1.000t of NaOH and 1.658t of HNO_3. The energy required for the separation and transportation of materials in the process is neglected in the calculation of heat requirement.

The theoretical heat requirement for the manufacture of NaOH is calculated as 10.2 kcal/mol[10] the case of the electrolysis process of NaCl. Here, the heat of 10.2 kcal/mol does not include the heat required for the manufacture of accompanying Cl_2 with NaOH. If the fossil fuel equivalent to electrical energy is assumed to be three times the amount of the electrical energy delivered to the electrolysis process of NaCl, the theoretical heat requirement for the manufacture of NaOH is 0.765×10^6 kcal/*t*-NaOH. On the other hand, nitric acid is mostly manufactured *via* oxidation of ammonia. Ammonia is currently synthesized *via* the reaction between hydrogen from naphtha and nitrogen from air. The heat requirement for this synthesis is expected to be 4.03×10^6 kcal/*t*-NH_3.[11] The heat requirement for the manufacture of HNO_3 from NH_3 is assumed to be negligibly small in this discussion. Thus, the overall heat requirement for the manufacture of 1.658 t of HNO_3 is 1.80×10^6 kcal. As a result, the total heat requirement for the manufacture of 1.000 t of NaOH and 1.658 t of HNO_3 is estimated to be at least 2.56×10^6 kcal for the current manufacturing processes of NaOH and HNO_3. This value of heat requirement corresponds approximately to the case of thermal regeneration of as low as 5% in the process of this study, as is clear from Fig. 10. If thermal regeneration is practised to more than 5% in this thermochemical process, this process might be a more energy-saving process than the current manufacturing processes of NaOH and HNO_3.

Conclusion

1) A new thermochemical process for manufacture of NaOH and HNO_3 from $NaNO_3$ has successfully been devised which essentially comprises a combination of a splitting of $NaNO_3$ by Fe_2O_3 and a hydrolysis of $NaFeO_2$.

2) The feasibility of the two key reactions, (i) the splitting of $NaNO_3$ by Fe_2O_3 and (ii) the hydrolysis of $NaFeO_2$, has experimentally been verified. The conversion rate is 100% for reaction (i) at 1050 K and more than 98% for reaction (ii) at 343 K. Sufficiently high reaction rates are available for both the reactions.

3) A material and heat flow-sheet of the process has been constructed which is simple as shown in Fig. 9.

4) This proposed thermochemical process is expected to be more energy-saving than the current processes of manufacturing NaOH and HNO_3, if heat regeneration is practised to more than 5% in the process of this study.

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